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DE-A- 1 808 388
DE-A- 2 543 272
DE-A- 2 721 058
FR-A- 2 171 278
FR-A- 2 303 813
FR-A- 2 347 388
FR-A- 2 348 231
GB-A- 1 258 984
GB-A- 1 355 245
US-A- 632 416
US-A- 3 644 318
US-A- 3 666 736
US-A- 4 003 712
US-A- 4 048 412

(56) References cited:

US-A- 4 076 698
Kirk Othmer Encyclopedia of Chemical Technology, Vol. 14, 2nd Edition, 1967, pp. 246-251
Journal of Polymer Science, Part B, Polymer Physics, Vol. 26, 1988, pp. 1995-2005

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EP 0 004 651 B2

Description

This invention relates to the use of ethylene hydrocarbon copolymers for preparing articles by injection molding and roto molding.

5 There is currently a need for molded plastic articles such as, for example, lids, closures, food and garbage containers, bottles, dishpans and toys which provide stress crack resistance when in contact with detergents, vegetable oils and fats, and/or which have superior impact strength at low temperatures (i.e. $\leq 0^\circ\text{C}$).

Attempts have been made to mold these articles from high pressure ethylene homopolymers, or from blends of high density polyethylene and copolymers of ethylene and polar comonomers such as vinyl acetate or ethyl acrylate.

10 However, the articles molded from high pressure polyethylenes have insufficient stress crack resistance and low temperature impact strength. The polar copolymer blends with high density polyethylene, though better than the high pressure polyethylenes in these properties, are very expensive to produce, are less translucent, have more odor, poorer electrical properties, a high hexane extractable level and are more prone to exhibit color segregation when compounded with pigments.

GB-A-1 258 984 deals with a suspension polymerization for the production of homo- and copolymers of olefins in which the precursor from the magnesium compound and the titanium compound were either activated completely outside of the reaction medium or activated completely in the reaction medium. The obtained polymers shall have a narrow molecular weight distribution (M_w/M_n between 2 and 4), the most important property of the polymers is their excellent color and corrosion values. Nothing is contained in this reference which shows that by different catalysts, a different activation of the catalyst and in a gas phase fluid bed process polymers may be obtained which have especially valuable properties, as it is shown below in the various tables.

It has now been unexpectedly found that articles molded from ethylene hydrocarbon copolymers obtainable as herein described have superior stress crack resistance and low temperature properties.

25 Additionally, articles injection molded from such ethylene hydrocarbon copolymers have high surface gloss and are free from dull swirls. Further, articles molded from said copolymers have excellent flex life, particularly when flexed across the direction of orientation.

An object of the present invention is to provide molded articles of ethylene hydrocarbon copolymers having superior stress crack resistance and low temperature properties.

30 A further object of the present invention is to provide articles injection molded from ethylene hydrocarbon copolymers of high gloss and essentially free from dull swirls.

Another object of the present invention is to provide articles molded from ethylene hydrocarbon copolymer which have low warpage.

35 Another object of the present invention is to provide articles molded from ethylene hydrocarbon copolymer of superior flex life.

It has now been found that articles molded from ethylene hydrocarbon copolymers obtainable as herein described have superior stress crack resistance, low temperature properties and flex life, have high gloss, low warpage and are essentially free from dull swirls.

40 The present invention relates to the use of low density ethylene hydrocarbon copolymer containing ≥ 90 mol percent of ethylene and ≤ 10 mol percent of propylene and/or butene-1 and having a density of ≥ 0.91 to ≤ 0.94 g/cm³, a melt index of 7 to 100 g/min a molecular weight distribution M_w/M_n in the range of from 2.7 to 4.1, a total unsaturation group content of from 0.1 to 0.3 C = C/1000 carbon atoms, and a secant modulus of ≥ 100 to ≤ 5600 bar ($\geq 30,000$ to $\leq 80,000$ psi), and obtainable by copolymerizing ethylene with propylene and/or butene-1 at a temperature of from about 30° to 115°C in a gas phase containing from 0 to 2.0 moles of hydrogen per mol of ethylene in the presence of particles of an activated precursor composition wherein said precursor composition has the formula



50 wherein

m is ≥ 1.5 to ≤ 56

n is 0 or 1

p is ≥ 6 to ≤ 116

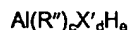
55 q is ≥ 2 to ≤ 85

R is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical, or COR' wherein R' is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical,

X is selected from the group consisting of Cl, Br, I or mixtures thereof ;

ED is a liquid organic electron donor compound in which said precursor composition and the Ti and Mg components thereof are soluble and which is selected from the group consisting of alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ethers, cyclic ethers and aliphatic ketones,

said precursor composition having an average particle size of 10 to 100 μm , a bulk density of 0.29 to 0.53 g/cm^3 , and being mechanically mixed or blended with at least one solid inert carrier material in a ratio of 0.033 to 1 part of precursor composition per part by weight carrier material, and being activated with an activator compound having the formula



10

wherein

X' is Cl or OR''', R'' and R''' are the same or different and are C₁ to C₁₄ saturated hydrocarbon radicals,

d is 0 to 1.5,

15

e is 0 or 1, and

c + d + e = 3

which polymerization is conducted continuously in a gas phase fluid bed reaction zone under a pressure of < 69 bar (< 1000 psi) and said precursor composition is partially activated with > 0 to < 10 mols of activator compound per mol of titanium compound in said precursor composition in a hydrocarbon slurry prior to feeding of the precursor composition to said reaction zone, dried to obtain a free-flowing solid particulate material, and then being completely activated in said reaction zone with ≥ 10 up to a total of ≤ 400 mol of activator compound per mol of titanium compound in said precursor composition, said complete activation being effected by spraying additional activator compound into the reactor in the form of a solution in a hydrocarbon containing 2 to 30 weight percent of the activator compound, or absorbed on a carrier material containing 10 to 50 weight percent of the activator compound ;

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for preparing articles by injection molding and roto molding.

The copolymers which may be used in the present invention are copolymers of a major mol percent ($\geq 90\%$) of ethylene, and a minor mol percent ($\leq 10\%$) of propylene and/or butene-1.

The copolymers used in the present invention have a melt flow ratio of ≥ 22 to ≤ 32 , and preferably of ≥ 25 to ≤ 30 . The melt flow ratio value is another means of indicating the molecular weight distribution of a polymer. The melt flow ratio (MFR) range of ≥ 22 to ≤ 32 thus corresponds to a M_w/M_n value range of 2.7 to 4.1 and the MFR range of ≥ 25 to ≤ 30 corresponds to a M_w/M_n range of 2.8 to 3.6.

The melt index of a copolymer is a reflection of its molecular weight. Polymers having a relatively high molecular weight have a relatively low melt index. Ultrahigh molecular weight ethylene polymers have a high load (HLMI) melt index of about 0.0 g/10 min, and very high molecular weight polymers have a high load melt index (HLMI) of about 0.0 to 1.0 g/10 min. Such high molecular weight polymers are difficult, if not impossible, to mold in conventional injection molding equipment. The polymers used in the present invention, on the other hand, can be readily molded in such equipment. They have a standard or normal load melt index of 7 to 100 g/10 min, and preferably of 7 to 80 g/10 min, and a high load melt index (HLMI) of 11 to 2000 g/10 min. The melt index of the copolymers which are used in the present invention is a function of a combination of the polymerization temperature of the reaction employed in their preparation, the density of the copolymer and the hydrogen/monomer ratio in the reaction system. Thus, the melt index is raised by increasing the polymerization temperature and/or by decreasing the density of the polymer and/or by increasing the hydrogen/monomer ratio. In addition to hydrogen, other chain transfer agents, such as dialkyl zinc compounds, may also be used to further increase the melt index of the copolymers.

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The copolymers used in the present invention have an unsaturated group content of ≥ 0.1 to ≤ 0.3 , C = C/1000 carbon atoms.

The copolymers used in the present invention have a n-hexane extractable content (at 50°C) of less than about 3 and, preferably, of less than about 2, weight percent.

50

The copolymers used in the present invention have a residual catalyst content, in terms of parts per million of titanium metal, of the order of > 0 to < 20 parts per million (ppm) at a productivity level of $\geq 50,000$ kg of polymer per kg of titanium, and of the order of > 0 to ≤ 10 ppm at a productivity level of $\geq 100,000$ kg of polymer per kg of titanium, and of the order of > 0 to ≤ 3 parts per million at a productivity level of $\geq 300,000$ kg of polymer per kg of titanium. (In terms of Cl, Br or I residues, the copolymers used in the present invention have a Cl, Br or I residue content which depends upon the Cl, Br or I content of the precursor. From the Ti to Cl, Br or I ratio in the initial precursor, it is possible to calculate Cl, Br, or I residues from knowledge of the productivity level based on titanium residue only. For many of the copolymers made only with Cl containing components of the catalyst system (Cl/Ti = 7), one can calculate a Cl residue content of > 0 to ≤ 140 ppm at a productivity of \geq

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50,000 kg of polymer per kg of titanium, a Cl content of > 0 to ≤ 70 ppm at a productivity of $\geq 100,000$ kg of polymer per kg of titanium, and a Cl content of > 0 to ≤ 20 ppm at a productivity of $\geq 300,000$ kg of polymer per kg of titanium. The copolymers are readily produced at productivities of up to about 1,000,000 kg of polymer per kg of titanium.

5 The copolymers used in the present invention are granular materials which have an average particle size of the order of 0.13 to 1.78 mm (0.005 to 0.07 inches), and preferably of 0.5 to 1.00 mm (0.02 to 0.04 inches) in diameter. The particle size is important for the purpose of readily fluidizing the polymer particles in the fluid bed reactor, as described below. The copolymers used in the present invention have a bulk density of 240 to 500 kg/m³ (15 to 31 pounds per cubic foot).

10 For the molding of articles, such as lids, closures, food and garbage containers, dishpans, hinges and toys, which must have excellent stress crack resistance and/or low temperature toughness, gloss or long flex life, the preferred copolymers used in the present invention are those having a density of ≥ 0.918 to ≤ 0.935 g/cm³, a molecular weight distribution Mw/Mn of 2.7 to 4.1, a standard melt index of 7 to 100 g/10 min, and preferably of 7 to 80 g/10 min, and secant modulus 207 to 551 N/mm² (30,000 to 80,000 psi).

15 The copolymers employed herein may be produced in accordance with procedures as set forth in EP-A-4645 and 4647, as well as the procedures set forth below which will produce ethylene hydrocarbon copolymers with the properties as heretofore described.

The copolymers can be readily produced in a low pressure gas phase fluid bed reaction process, as disclosed below, if the monomer charge is polymerized under a specific set of operating conditions, as disclosed below, and in the presence of a specific high activity catalyst, which is also described below.

20 The compounds used to form the high activity catalyst which may be used to prepare the copolymers employed in the present invention comprise at least one titanium compound, at least one magnesium compound, at least one electron donor compound, at least one activator compound, and at least one inert carrier material, as defined below.

25 The titanium compound has the structure



wherein R is a C₁ to C₁₄ aliphatic or aromatic hydrocarbon radical, or COR' where R' is a C₁ to C₁₄ aliphatic or aromatic hydrocarbon radical,

30 X is selected from the group consisting of Cl, Br, I, or mixtures thereof, a is 0 or 1, b is 2 to 4 inclusive and a + b = 3 or 4.

The titanium compounds can be used individually or in combinations thereof, and would include

35 TiCl_3 , TiCl_4 , $\text{Ti}(\text{OCH}_3)\text{Cl}_3$, $\text{Ti}(\text{OC}_6\text{H}_5)\text{Cl}_3$,

$\text{Ti}(\text{OCOCH}_3)\text{Cl}_3$ and $\text{Ti}(\text{OCOC}_6\text{H}_5)\text{Cl}_3$.

Accordingly the titanium compound contains preferably up to 7 carbon atoms.

40 The magnesium compound has the structure



45 wherein X is selected from the group consisting of Cl, Br, I, or mixtures thereof. Such magnesium compounds can be used individually or in combinations thereof and would include MgCl_2 , MgBr_2 and MgI_2 . Anhydrous MgCl_2 is the particularly preferred magnesium compound.

From 1.5 to 56, and preferably from 1.5 to 10, mols of the magnesium compound are used per mol of the titanium compound in preparing the catalysts employed in the present invention.

50 The titanium compound and the magnesium compound should be used in a form which will facilitate their dissolution in the electron donor compound, as described herein below.

The electron donor compound is an organic compound which is liquid at 25°C and in which the titanium compound and the magnesium compound are partially or completely soluble. The electron donor compounds are known as such, or as Lewis bases.

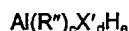
55 The electron donor compounds would include such compounds as alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ethers, cyclic ethers and aliphatic ketones. Among these electron donor compounds the preferable ones are alkyl esters of C₁ to C₄ saturated aliphatic carboxylic acids; alkyl esters C₇ to C₈ aromatic carboxylic acids; C₂ to C₈, and most preferably C₃ to C₄, aliphatic ethers; C₃ to C₄ cyclic ethers, and most

preferably C₄ cyclic mono- or di-ethers; C₃ to C₈, and most preferably C₃ to C₄, aliphatic ketones. The most preferred of these electron donor compounds would include methyl formate, ethyl acetate, butyl acetate, ethyl ether, hexyl ether, tetrahydrofuran, dioxane, acetone and methyl isobutyl ketone.

The electron donor compounds can be used individually or in combinations thereof.

5 From 2 to 85, and preferably from 3 to 10 mols of the electron donor compound are used per mol of Ti.

The activator compound has the structure

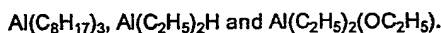
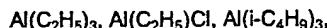


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wherein X' is Cl or OR''', R'', and R''' are the same or different and are C₁ to C₁₄ saturated hydrocarbon radicals, d is 0 to 1.5, e is 1 or 0 and c + d + e = 3.

Such activator compounds can be used individually or in combinations thereof and would include

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Accordingly each of the substituents R'' and R''' of the activator compounds contain preferably up to 8 carbon atoms.

From 10 to 400, and preferably from 10 to 100, mols of the activator compound are used per mol of the titanium compound in activating the precursor composition.

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The carrier materials are solid, particulate materials which are inert to the other components of the catalyst composition, and to the other active components of the reaction system. These carrier materials would include inorganic materials such as oxides of silicon and aluminum and molecular sieves, and organic materials such as olefin polymers such as polyethylene. The carrier materials are used in the form of dry powders having an average particle size of 10 to 250 μm, preferably of 50 to 150 μm. These materials are also preferably porous and have a surface area of ≥ 3 m²g⁻¹, preferably of ≥ 50 square meters per gram. The carrier material should be dry, that is, free of absorbed water. Drying of the silica carrier material is carried out by heating it at a temperature of ≥ 600°C. Alternatively, the silica carrier material dried at a temperature of ≥ 200°C may be treated with 1 to 8 weight percent of one or more of the aluminum alkyl compounds described above. This modification of the silica carrier material by the aluminum alkyl compound provides the catalyst composition with increased activity and also improves polymer particle morphology of the resulting ethylene polymers.

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The catalyst which may be used to prepare the copolymers employed in the present invention is prepared by first preparing a precursor composition from the titanium compound, the magnesium compound, and the electron donor compound in one or more steps as described below, and by then treating the precursor composition with the carrier material and the activator compound as described below.

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The precursor composition is formed by dissolving the titanium compound and the magnesium compound in the electron donor compound at a temperature of 20°C up to the boiling point of the electron donor compound. The titanium compound can be added to the electron donor compound before or after the addition of the magnesium compound, or concurrent therewith. The dissolution of the titanium compound and the magnesium compound can be facilitated by stirring, and, in some instances by refluxing, these two compounds in the electron donor compound. When the titanium compound and the magnesium compound are dissolved, the precursor composition is isolated by crystallization or by precipitation with a C₅ to C₈ aliphatic or aromatic hydrocarbon such as hexane, isopentane or benzene.

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The crystallized or precipitated precursor composition is isolated in the form of fine, free flowing particles having an average particle size of 10 to 100 μm and a settled bulk density of 290 to 530 kg/m³ (18 to 33 pounds per cubic foot).

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Particle sizes of ≤ 100 μm are preferred for use in a fluid bed process. The particle size of the isolated precursor composition can be controlled by the rate of crystallization or precipitation.

When thus made as disclosed above, the precursor composition has the formula

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wherein

ED is the electron donor compound,
 m is ≥ 1.5 to ≤ 56 , and preferably ≥ 1.5 to ≤ 5.0 ,
 n is 0 to 1,

p is ≥ 6 to ≤ 116 , and preferably ≥ 6 to ≤ 14 ,

5 q is ≥ 2 to ≤ 85 , and preferably ≥ 4 to ≤ 11 ,

R is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical, or COR' wherein R' is a C_1 to C_{14} aliphatic or aromatic hydrocarbon radical and,

X is selected from the group consisting of Cl, Br, I, or mixtures thereof.

10 The polymerization activity of the completely activated catalyst is so high in the polymerization process described herein that a dilution of the precursor composition with the carrier material is necessary in order to effectively control the reaction rate. The dilution of the precursor composition can be accomplished before the precursor composition is partially activated, as disclosed below, or concurrent with such activation. The dilution of the precursor composition with the carrier material is accomplished by mechanically mixing or blending 0.033 to 1, and preferably 0.1 to 0.33, parts of the precursor composition with one part by weight of the carrier material.

15 In order to be used in the preparation of the copolymers employed in the present invention, the precursor composition must be treated with sufficient activator compound to transform the Ti atoms in the precursor composition to an active state. It has been found, however, that the manner of activating the catalyst is very critical in order to obtain an active material, even when an inert carrier is present. Attempts to activate the catalyst by a process similar to that of US-A-3,989,881, for example, wherein the total amount of activator theoretically needed to fully activate the catalyst was added to the precursor composition in a hydrocarbon slurry, followed by drying of the slurry at temperatures of ≥ 20 to $\leq 80^\circ\text{C}$ to remove the solvent therefrom to facilitate the use of the catalyst in a gas phase fluid bed process, produced a product which was not sufficiently active in the process otherwise described below for commercial purposes.

20 It has been found that, in order to prepare a useful catalyst it is necessary to conduct the activation in such a way that the final activation is conducted in such manner as to avoid the need for drying the fully active catalyst to remove solvent therefrom.

25 Accordingly, the precursor composition is first partially activated outside the polymerization reactor by treating it in a hydrocarbon solvent slurry with > 0 to < 10 , preferably 4 to 8, mols of activator compound per mol of titanium compound in said precursor composition. The hydrocarbon solvent is then removed by drying and the partially activated precursor composition is fed to the polymerization reactor where activation is completed by treatment with additional activator compound.

30 In the first stage of the activation the solid particulate precursor composition, diluted with carrier material, is reacted with and partially activated by enough activator compound so as to provide a partially activated precursor composition which has an activator compound/Ti molar ratio of > 0 to $< 10 : 1$, and preferably of 4 to 8: 1. This partial activation reaction is carried out in a hydrocarbon slurry followed by drying of the resulting mixture, to remove the solvent, at temperatures between 20 to 80, and preferably of 50 to 70°C . The resulting product is a freeflowing solid particulate material which can be readily fed to the polymerization reactor. The partially activated precursor composition, however, is, at best, weakly active as a polymerization catalyst. In order to render the partially activated precursor composition active for ethylene polymerization purposes, additional activator compound must also be added to the polymerization reactor to complete, in the reactor, the activation of the precursor composition. The additional activator compound and the partially activated precursor composition are preferably fed to the reactor through separate feed lines. The additional activator compound may be sprayed into the reactor in the form of a solution thereof in a hydrocarbon solvent such as isopentane, hexane, or mineral oil. This solution usually contains 2 to 30 weight percent of the activator compound. The activator compound may also be added to the reactor in solid form, by being absorbed on a carrier material. The carrier material usually contains 10 to 50 weight percent of the activator for this purpose. The additional activator compound is added to the reactor in such amounts as to provide, in the reactor, with the amounts of activator compound and titanium compound fed with the partially activated precursor composition, from ≥ 10 to ≤ 400 total mols of activator compound per mol of titanium compound in said precursor composition, preferably from 15 to 60 total mols of activator compound per mol of titanium compound in said precursor composition. The additional amounts of activator compound added to the reactor react with, and complete the activation of, the precursor composition in the reactor.

40 In the continuous gas phase fluid bed process disclosed below, discrete portions of the catalyst, i.e. the partially activated precursor composition and the additional activator compound needed to complete the activation thereof, is continuously fed to the reactor during the continuing polymerization process in order to replace active catalyst sites that are expended during the course of the process.

55 The polymerization reaction is conducted by contacting a stream of the monomers, in the fluid bed process described below, and substantially in the absence of catalyst poisons such as moisture, oxygen, CO, CO_2 , and

acetylene with a catalytically effective amount of the catalyst at a temperature and at a pressure sufficient to initiate the polymerization reaction.

In order to achieve the desired density ranges in the copolymers it is necessary to copolymerize enough of the comonomers with ethylene to achieve a level of ≥ 1 to 10 mol percent of the comonomer in the copolymer.

5 The amount of comonomer needed to achieve this result will depend on the particular comonomer(s) employed. There is provided below a listing of the amounts, in moles, of the comonomers that must be copolymerized with ethylene in order to provide polymers having the desired density range at any given melt index. The listing also indicates the relative molar concentration, of such comonomer to ethylene, which must be present in the gas stream of monomers which is fed to the reactor.

10

Comonomer	mol % needed in copolymer	Gas stream comonomer/ethylene molar ratio
15 propylene	3.0 to 10	0.2 to 0.9
butene-1	2.5 to 7.0	0.2 to 0.7

20 A fluidized bed reaction system which can be used to prepare the copolymers employed in the practice of the process of the present invention is illustrated in Figure 1. With reference thereto the reactor 10 consists of a reaction zone 12 and a velocity reduction zone 14.

The reaction zone 12 comprises a bed of growing polymer particles, formed polymer particles and a minor amount of catalyst particles fluidized by the continuous flow of polymerizable and modifying gaseous components in the form of make-up feed and recycle gas through the reaction zone. To maintain a viable fluidized bed, the mass gas flow rate through the bed must be above the minimum flow required for fluidization, and preferably from 1.5 to 10 times G_{mf} and more preferably from 3 to 6 times G_{mf} . G_{mf} is used in the accepted form as the abbreviation for the minimum mass gas flow required to achieve fluidization, C. y. Wen and Y. H. Yu, "Mechanics of Fluidization", Chemical Engineering Progress Symposium Series, Vol. 62, p. 100-111 (1966).

25 It is essential that the bed always contains particles to prevent the formation of localized "hot spots" and to entrap and distribute the particulate catalyst throughout the reaction zone. On start up, the reaction zone is usually charged with a base of particulate polymer particles before gas flow is initiated. Such particles may be identical in nature to the polymer to be formed or different therefrom. When different, they are withdrawn with the desired formed polymer particles as the first product. Eventually, a fluidized bed of the desired polymer particles supplants the start-up bed.

30 The partially activated precursor compound used in the fluidized bed is preferably stored for service in a reservoir 32 under a blanket of a gas which is inert to the stored material, such as nitrogen and argon.

Fluidization is achieved by a high rate of gas recycle to and through the bed, typically in the order of 50 times the rate of feed of make-up gas. The fluidized bed has the general appearance of a dense mass of viable particles in possible free-vortex flow as created by the percolation of gas through the bed. The pressure drop through the bed is equal to or slightly greater than the mass of the bed divided by the cross-sectional area. It is thus dependent on the geometry of the reactor.

35 Make-up gas is fed to the bed at a rate equal to the rate at which particulate polymer product is withdrawn. The composition of the make-up gas is determined by a gas analyzer 16 positioned above the bed. The gas analyzer determines the composition of the gas being recycled and the composition of the make-up gas is adjusted accordingly to maintain an essentially steady state gaseous composition within the reaction zone.

40 To insure complete fluidization, the recycle gas and, where desired, part of the make-up gas are returned to the reactor at point 18 below the bed. There exists a gas distribution plate 20 above the point of return to aid fluidizing the bed.

The portion of the gas stream which does not react in the bed constitutes the recycle gas which is removed from the polymerization zone, preferably by passing it into a velocity reduction zone 14 above the bed where entrained particles are given an opportunity to drop back into the bed. Particle return may be aided by a cyclone 22 which may be part of the velocity reduction zone or exterior thereto. Where desired, the recycle gas may then be passed through a filter 24 designed to remove small particles at high gas flow rates to prevent dust from contracting heat transfer surfaces and compressor blades.

55 The recycle gas is then compressed in a compressor 25 and then passed through a heat exchanger 26 wherein it is stripped of heat of reaction before it is returned to the bed. By constantly removing heat of reaction, no noticeable temperature gradient appears to exist within the upper portion of the bed. A temperature gradient will exist in the bottom of the bed in a layer of 15 to 30 cm (6 to 12 inches), between the temperature of the

inlet gas and the temperature of the remainder of the bed. Thus, it has been observed that the bed acts to almost immediately adjust the temperature of the recycle gas above this bottom layer of the bed zone to make it conform to the temperature of the remainder of the bed, thereby maintaining itself at an essentially constant temperature under steady state conditions. The recycle is then returned to the reactor at its base 18 and to the fluidized bed through distribution plate 20. The compressor 25 can also be placed downstream of the heat exchanger 26.

The distribution plate 20 plays an important role in the operation of the reactor. The fluidized bed contains growing and formed particulate polymer particles as well as catalyst particles. As the polymer particles are hot and possibly active, they must be prevented from settling, for if a quiescent mass is allowed to exist, any active catalyst contained therein may continue to react and cause fusion. Diffusing recycle gas through the bed at a rate sufficient to maintain fluidization at the base of the bed is, therefore, important. The distribution plate 20 serves this purpose and may be a screen, slotted plate, perforated plate, a plate of the bubble cap type, and the like. The elements of the plate may all be stationary, or the plate may be of the mobile type disclosed in US-A-3,298,792. Whatever its design, it must diffuse the recycle gas through the particles at the base of the bed to keep them in a fluidized condition, and also serve to support a quiescent bed of resin particles when the reactor is not in operation. The mobile elements of the plate may be used to dislodge any polymer particles entrapped in or on the plate.

Hydrogen may be used as a chain transfer agent in the polymerization reaction. The ratio of hydrogen/ethylene employed will vary between 0 to 2.0 moles of hydrogen per mole of the monomer in the gas stream.

Any gas inert to the catalyst and reactants can also be present in the gas stream. The activator compound is preferably added to the reaction system at the hottest portion of the gas, which is usually downstream from heat exchanger 26. Thus, the activator may be fed into the gas recycle system from dispenser 27 through line 27A.

Compounds of the structure $Zn(R_a)(R_b)$, wherein R_a and R_b are the same or different C_1 to C_{14} aliphatic or aromatic hydrocarbon radicals, may be used in conjunction with hydrogen, with the catalysts disclosed herein as molecular weight control or chain transfer agents, that is, to increase the melt index values of the copolymers that are produced. From 0 to 50, and preferably from 20 to 30, mols of the Zn compound would be used in the gas stream in the reactor per mol of titanium compound in the reactor. The zinc compound would be introduced into the reactor, preferably in the form of a dilute solution (2 to 30 weight percent) in hydrocarbon solvent or absorbed on a solid carrier material, such as silica, of the types described above, in amounts of from 10 to 50 weight percent. These compositions tend to be pyrophoric. The zinc compound may be added alone, or with any additional portions of the activator compound that are to be added to the reactor from a feeder, not shown, which could be positioned adjacent dispenser 27, near the hottest portion of the gas recycle system.

It is essential to operate the fluid bed reactor at a temperature below the sintering temperature of the polymer particles. To insure that sintering will not occur, operating temperatures below the sintering temperature are desired. For the production of ethylene copolymers an operating, temperature of from 30 to 115°C is preferred, and a temperature of from 75 to 95°C is most preferred. Temperatures of 75 to 95°C are used to prepare products having a density of from 0.91 to 0.92 g/cm³, and temperatures of from 80 to 100°C are used to prepare products having a density of from > 0.92 to 0.94 g/cm³.

The fluid bed reactor is operated at pressures of up to 69 bar (1000 psi), and is preferably operated at a pressure of from 10.3 to 24 bar (150 to 350 psi), with operation at the higher pressures in such ranges favoring heat transfer since an increase in pressure increases the unit volume heat capacity of the gas.

The partially activated precursor composition is injected into the bed at a rate equal to its consumption at a point 30 which is above the distribution plate 20. Injecting the precursor composition at a point above the distribution plate is an important feature of this invention. Since the catalysts used to prepare the copolymers employed in the invention are highly active, injection of the precursor composition into the area below the distribution plate may cause polymerization to begin there and eventually cause plugging of the distribution plate. Injection into the viable bed, instead, aids in distributing the catalyst throughout the bed and tends to preclude the formation of localized spots of high catalyst concentration which may result in the formation of "hot spots".

A gas which is inert to the catalyst, such as nitrogen or argon, is used to carry the partially activated precursor composition, and any additional activator compound or non-gaseous chain transfer agent that is needed, into the bed.

The production rate is controlled by the rate of catalyst injection. The production rate may be increased by simply increasing the rate of catalyst injection and decreased by reducing the rate of catalyst injection.

Since any change in the rate of catalyst injection will change the rate of generation of the heat of reaction, the temperature of the recycle gas is adjusted upwards or downwards to accommodate the change in rate of heat generation. This insures the maintenance of an essentially constant temperature in the bed. Complete instrumentation of both the fluidized bed and the recycle gas cooling system, is, of course, necessary to detect

any temperature change in the bed so as to enable the operator to make a suitable adjustment in the temperature of the recycle gas.

Under a given set of operating conditions, the fluidized bed is maintained at essentially a constant height by withdrawing a portion of the bed as product at a rate equal to the rate of formation of the particulate polymer product. Since the rate of heat generation is directly related to product formation, a measurement of the temperature rise of the gas across the reactor (the difference between inlet gas temperature and exit gas temperature) is determinative of the rate of particulate polymer formation at a constant gas velocity.

The particulate polymer product is preferably continuously withdrawn at a point 34 at or close to the distribution plate 20, and in suspension with a portion of the gas stream which is vented before the particles settle to preclude further polymerization and sintering when the particles reach their ultimate collection zone. The suspending gas may also be used, as mentioned above, to drive the product of one reactor to another reactor.

The particulate polymer product is conveniently and preferably withdrawn through the sequential operation of a pair of timed valves 36 and 38 defining a segregation zone 40. While valve 38 is closed, valve 36 is opened to emit a plug of gas and product to the zone 40 between it and valve 36 which is then closed. Valve 38 is then opened to deliver the product to an external recovery zone. Valve 38 is then closed to await the next product recovery operation.

Finally, the fluidized bed reactor is equipped with an adequate venting system to allow venting the bed during start up and shut down. The reactor does not require the use of stirring means and/or wall scraping means.

The highly active catalyst system employed to prepare the copolymers employed in this invention appears to yield a fluid bed product having an average particle size between 0.125 to 1.78 mm (0.005 to 0.07 inches) and preferably 0.5 to 1.0 mm (0.02 to 0.04 inches).

The feed stream of gaseous monomer, with or without inert gaseous diluents, is fed into the reactor so as to maintain a space time yield of 32 to 160 kg/h/m³ (2 to 10 pounds/hour/cubic foot) of bed volume.

The polymer directly recovered from the polymerization reactor is in granular form ("virgin" copolymer).

Additives such as fillers, pigments, stabilizers, antioxidants, lubricants, flame retardants, UV absorbers, plasticizers and foaming agents may be added to the copolymers herein in amounts which will produce the intended effect.

The articles obtainable according to the present invention are produced by injection molding and roto molding.

Articles such as lids, closures, food or garbage containers, dishpans and toys are produced by ram or screw injection molding processes well known in the art. For example, Renfrew & Morgan, "Polythene", second edition, Interscience Publisher, (1960) pages 549-570, describes injection molding of polyethylene. The articles of the present invention are molded in a standard injection molding machine where the copolymer is heated at a temperature of from 180° to 270°C in the machine until plasticized and is then injected at a gauge pressure of from 31 to 140 bar (500 to 2000 psi) into a mold cavity of desired configuration. The copolymer is cooled in the mold cavity at temperatures of from 15° to 60°C until it conforms to the shape of the mold cavity. The molded article is then removed from the mold.

Articles such as bottles and containers are molded by injection molding processes which are well known in the prior art. For example, Renfrew Morgan, *supra*, pages 571 to 579, describe blow molding of polyethylene.

Articles such as large toys and industrial size food and garbage containers are principally made by rotomolding instead of injection molding, because of the intricate shapes involved and the superior economics the process offers for low volume production.

The process of rotomolding is well known in the art and is described in "Encyclopedia of Polymer Science and Technology", Volume 9, Interscience Publisher, 1968, pages 118-137.

In this process either powdered resin or fine resin particles are placed into the metal mold cavity which is then rotated in a hot oven 260 to 315°C (500 to 600°F) until the resin melts and coats the inside of the mold cavity. The metal mold containing the molten resin is then transferred to a cooling means wherein it is cooled until the molten resin has solidified and conformed to the shape of the mold cavity.

Before processing according to the methods heretofore described, the copolymer may be mixed or blended with various additives and then added to the molding machine, or the copolymer may be added directly to the molding machine together with any additives.

The shaped articles obtainable according to the present invention molded from ethylene hydrocarbon copolymers include lids, closures, food and garbage containers, dishpans, bottles, toys and hinges.

The articles may be subjected to any further treatment such as coating or painting, as desired, depending upon the ultimate use of the article.

Examples

The following examples are designed to illustrate the present invention and are not intended as a limitation on the scope thereof.

5 The properties of the polymers herein were determined by the following test methods.

Density	ASTM D-1505-Plaque is conditioned for one hour at 100°C to approach equilibrium crystallinity-Reported as grams per cubic centimeter (g/cm ³). All density measurements are made in a density gradient column.
10 Melt Index (MI)	ASTM D-1238-Condition E-measured at 190°C-reported as grams per 10 minutes.
Flow Rate (HLMI)	ASTM D-1238-Condition F-measured at 10 times the weight used in the melt index test above.
Melt Flow Ratio (MFR)= 15 Molecular Weight Distribution, $\overline{M}_w/\overline{M}_n$	Flow Rate/Melt Index Gel Permeation Chromatography Styragel Packing : Pore size packing sequence is 10 ⁶ , 10 ⁴ , 10 ³ , 10 ² , 6 nm. Solvent : Perchloroethylene at 117°C. Detection : Infrared at 3.41 μ m
20 Unsaturation	Infrared Spectrophotometer (Perkin Elmer Model 21) Pressings 0.64 mm (21 mils) in thickness are used. Absorbance is measured at 10.35 μ m for trans vinylene, 11.00 μ m for terminal vinyl, and 11.25 μ m for pendant vinylidene. The absorbance per mil at each wavelength is directly proportional to the product of unsaturation concentration and absorptivity. Absorptivities were taken from the literature values of deKock, R. J. and Hol., P., A., H., M., J. Poly. Sci., Part B, 2, 339 (1964)

25 Preparation of catalyst

Preparation of precursor composition.

In a 5 liter flask equipped with a mechanical stirrer, 16.0 g (0.168 Mol) of anhydrous MgCl₂ was mixed with 850 ml of pure tetrahydrofuran under nitrogen. The mixture was stirred at room temperature (~25°C) while
30 13.05 g (0.069 Mol) of TiCl₄ was added dropwise. After complete addition, the contents of the flask were heated to reflux for about 1/2 to 1 hour to dissolve the solids. The system was cooled to room temperature and 3 liters of pure n-hexane was slowly added over a period of 1/4 hours. A yellow solid precipitated. The supernatant liquid was decanted and the solids were washed three times with one liter of n-hexane. The solids were filtered and dried in a rotating evaporating flask at 40-60°C to give 55 g of solid precursor composition.

35 The precursor composition may be analyzed at this point for Mg and Ti content since some of the Mg and/or Ti compound may have been lost during the isolation of the precursor composition. The empirical formulas used herein in reporting these precursor compositions are derived by assuming that the Mg and the Ti still exist in the form of the compounds in which they were first added to the electron donor compound and that all other residual weight in the precursor composition is due to the electron donor compound.

40 Analysis of the solid showed the following :

Mg : 6.1% Ti : 4.9% ; which corresponds to TiMg_{2.45}Cl_{8.9}(THF)_{7.0}.

THF means tetrahydrofuran.

45 Activation procedure

The activation is conducted in such a way that the precursor composition is only partially activated prior to the introduction thereof into the polymerization reactor, and then the remainder of the activation process is completed within such reactor.

50 The desired weight of dry inert carrier material is charged to a mixing vessel or tank. For the examples described herein, the amount of inert carrier is 500 grams for silica and 1000 grams for a polyethylene carrier. The inert carrier material is then admixed with sufficient amounts of anhydrous, aliphatic hydrocarbon diluent, such as isopentane, to provide a slurry system. This usually requires 4 to 7 ml of diluent per gram of inert carrier. The desired weight of the precursor composition is then charged to the mixing vessel and thoroughly admixed with the slurry composition. The amount of precursor composition used in this procedure for making the catal-
55 ysts in these examples is 80 to 135 grams, with such precursor composition having an elemental titanium content of 1 \pm 0.1 millimole of Ti per gram of precursor composition.

The desired amount of activator compound needed to partially activate the precursor composition is added to the contents of the mixing vessel so as to partially activate the precursor composition. The amount of activator

compound used in this regard provides an Al/Ti ratio in the partially activated precursor composition of > 0 to $< 10 : 1$, and preferably of 4 to $8 : 1$. The activator compound is added to the mixing tank in the form of a solution which contains 20 weight percent of the activator compound (triethyl aluminum in these examples) in an inert aliphatic hydrocarbon solvent (hexane in these examples). The activation is accomplished by thoroughly mixing and contacting the activator compound with the precursor composition. All of the operations described above are conducted at room temperature, and at atmospheric pressure in an inert atmosphere.

The resulting slurry is then dried under a purge of dry inert gas, such as nitrogen or argon, at atmospheric pressure at a temperature of $\leq 60^\circ\text{C}$ to remove the hydrocarbon diluent. This process usually requires 3 to 5 hours. The resulting product is in the form of a dry free-flowing particulate material wherein the partially activated precursor composition is uniformly blended with the inert carrier. The dried non-pyrophoric product is stored under an inert gas.

In order to complete the activation of the partially activated precursor composition, additional activator compound is fed to the polymerization reactor absorbed on an inert carrier material, such as silica or polyethylene, or, most preferably, as a dilute solution in a hydrocarbon solvent such as isopentane.

When the activator compound is to be absorbed on a silica carrier, the two materials are mixed in a vessel containing about 4 ml of isopentane per gram of carrier material. The resulting slurry is then dried for about 3 to 5 hours under a purge of nitrogen at atmospheric pressure at a temperature of $65 \pm 10^\circ\text{C}$ to remove the hydrocarbon diluent. When the activator compound is to be injected into the polymerization reaction system as a dilute solution, concentrations of 5 to 10% by weight are preferred.

Regardless of the method used to introduce the activator compound into the polymerization reactor for the purpose of completing the activation of the precursor composition, it is added at a rate such as to maintain the Al/Ti ratio in the polymerization reactor at a level of ≥ 10 to $400 : 1$, and preferably of ≥ 10 to $100 : 1$.

Prior to being used herein, the silicas are dried at $\geq 200^\circ\text{C}$ for ≥ 4 hours.

Polymerization process, runs 1-8

Ethylene was copolymerized with propylene or butene-1 (propylene in Runs 1 and 2 and butene-1 in Runs 3 to 8) in each of this series of 8 Runs with catalyst formed and activated as described above to produce polymers having a density of 0.940 g/cm^3 . In each case, the partially activated precursor composition had an Al/Ti mol ratio of 4.4 to 5.8. The completion of the activation of the precursor composition in the polymerization reactor was accomplished with triethyl aluminum (as a 5 weight % solution in isopentane in Runs 1 and 2, and 4 to 8, and adsorbed on silica, 50/50 weight %, in Runs 3 so as to provide the completely activated catalyst in the reactor with an Al/Ti mol ratio of about 29 to 140.

Each of the polymerization reactions was continuously conducted for > 1 hour after equilibrium was reached and under a pressure of 22 bar (300 psig) and a gas mass flow of 5 to 6 times G_{mf} in a fluid bed reactor system at a space time yield of 48 to 128 kg/h/m^3 (3 to 8 lbs/h/ft³) of bed space. The reaction system was as described above. It has a lower section 3 m (10 feet) high and 34.3 cm (23 1/2 inches) in (inner) diameter, and an upper section which was 4.8 m (16 feet) high and 59.7 (23 1/2 inches) in (inner) diameter.

In several of the Runs zinc diethyl was added during the reaction (as a 2.6 weight % solution in isopentane) to maintain a constant Zn/Ti mol ratio. Where the zinc diethyl was used, the triethyl aluminum was also added as a 2.6 weight % solution in isopentane.

Table A below lists, with respect to Runs 1 to 8, various operating conditions employed in such Runs i.e., the weight % of precursor composition in the blend of silica and precursor composition ; Al/Ti ratio in the partially activated precursor composition ; Al/Ti ratio maintained in the reactor ; polymerization temperature ; % by volume of ethylene in reactor ; H_2 /ethylene mol ratio in the reactor ; and comonomer (C_x)/ C_2 mol ratio in reactor. Table B below lists properties of the granular copolymers directly obtained from the reactor ("virgin" resins) in runs 1 to 8, i.e. density ; melt index (M.I.) ; melt flow ratio (MFR) ; bulk density and average particle size.

TABLE A
Reaction conditions for runs 1 to 8

Run No.	Weight % precursor	Al/Ti ratio in part. act precursor	Al/Ti ratio in reactor	Temp °C	Vol % C ₂	H ₂ /C ₂ mol ratio	C _x /C ₂ mol ratio
1	8.3	5.8	40.5	90	41.7	0.492	0.486
2	8.3	5.8	50.8	90	39.7	0.566	0.534
3	19.8	4.40	26.7	85	50.2	0.350	0.350
4	8.3	5.8	124.6	90	45.1	0.456	0.390
5	8.3	5.8	80.8	90	42.7	0.365	0.396
6	8.3	5.8	52.2	90	48.4	0.350	0.397
7	8.3	5.8	140.1	90	42.6	0.518	0.393
8	8.3	5.8	63.5	90	40.8	0.556	0.391

TABLE B
Properties of polymers made in runs 1 to 8

Run No.	Density g/cm ³	M.I. g/10 min.	MFR	Bulk Density g/cm ³	(lb _x /ft ³)	Average particle size mm	(inches)
1	0.927	22.0	24.4	0.269	(16.8)	0.584	(0.0230)
2	0.929	24.0	23.4	0.280	(17.5)	0.584	(0.0230)
3	0.931	12.0	26.7	0.269	(16.8)	0.699	(0.0275)
4	0.929	16.0	24.1	0.277	(17.3)	0.584	(0.0230)
5	0.929	15.3	24.0	0.266	(16.6)	0.594	(0.0234)
6	0.928	11.5	24.1	0.267	(16.7)	0.630	(0.0248)
7	0.929	20.7	24.3	0.277	(17.3)	0.655	(0.0206)
8	0.929	29.2	26.1	0.269	(16.8)	0.523	(0.0206)

Control product 1

The control is a high pressure commercial polyethylene resin (Union Carbide DNDA 0415) produced in a stirred reactor at 1120 bar (16,000 psi) and 205°C.

Example 1

The resin produced in Run 1 and Control Product 1 were injection molded to form dishpans and lids.

The dishpans were injection molded on a 225 g (8 oz.) Impco® machine at a cylinder temperature of 260°C (500°F), an injection gauge pressure of 9.65 N/mm² (1400 psi) and a mold close time of 44 seconds. The other pertinent machine settings are as set forth in Table I.

The lids were injection molded on a 85 g (3 oz.) Moslo® ram machine at a material temperature of 285°C (545°F), a gauge pressure of 5.69 N/mm² (825 psi) and a mold close time of 15 seconds. the lids were center gated with an opening 0.75 mm (0.030 inches) in diameter, 0.75 mm (0.030 inches) long and were 15 cm (6 inches) in diameter, and 1 mm (0.040 inches) thick. The other pertinent conditions are listed in Table I.

TABLE I

	Machine type	Impco		Moslo	
	Injection Pressure N/mm ² (psi)	9.65 (1400)		5.69 (825)	
5	Cylinder Temperature, °C (°F)				
	Nozzle	260 (500)		260—288 (500—550)	
	Front	260 (500)		—	
10	Center	260 (500)		260—288 (500—550)	
	Rear	232 (450)		246—274 (475—525)	
	Mold Temperature, °C (°F)				
15	Movable	25.7 (80)		11.1 (52)	
	Stationary	23.9 (75)		11.1 (52)	
	Cycle, seconds				
	Injection	12		2—3	
20	Clamp (mold close time)	44		15	
	Booster	4		1.5	
	Prepack	4		2	
25	Gate Delay	12		—	
	Gate-to-Gate	72		18	

Each of the resins of Run 1 and Control Product 1 were tested for secant modulus of elasticity according to ASTM D368. Also, the melt index, density and melt flow ratio of these resins is as set forth in Table II.

The lids were tested for stress crack resistance in Crisco® oil. The lids were bent with the lips facing outside and opposite edges touching and stapled together. The bent section opposite the stapled edges was then immersed in Crisco® oil until cracking was observed. The results are as set forth in Table II.

The low temperature impact strength of the dishpans was measured at -51°C (-60°F) by dropping a 4.5 kg (10 pound) cylindrical dart with a 2.5 cm (1 inch) diameter hemispherical head onto the dishpan sprue area from increasing heights in 7.5 cm (3 inch) increments until the dishpan shattered or was punctured. The height at which failure occurred was multiplied by the dart weight and the result was reported in Nm (foot-pounds). The degree of warpage was determined by visual observations in comparison with the same part molded under the same conditions from the high pressure polyethylene resin of the same melt index and density.

The data shows that articles molded from the ethylene hydrocarbon copolymer obtainable as herein described have higher rigidity as shown by the secant modulus, excellent stress crack resistance, impact strength and warpage resistance, as compared to articles molded from high pressure polyethylene resin.

	Resin Properties	TABLE II	
		Run 1	Control product 1
5	Melt index, g/10 min.	20	20
	Density, g/cm ³	0.925	0.924
	Melt Flow Ratio	25	35
10	Properties of articles		
	Secant Modulus, N/mm ² (psi)	282 (41,000)	193 (28,000)
	Stress Crack Resistance, Time for Failure	>21 Days	3 Minutes
	Impact Strength at -51°C (-60°F) Nm (ft-lbs)	28.2 (20.8) (Punctured)	6.8 (5) (Shattered)
15	Warpage Resistance	Excellent	V. Good

Polymerization runs 9 to 12

Copolymers were prepared according to the procedure of Runs 1-8. The comonomer which was reacted with ethylene to produce the copolymer, and the melt index, density and melt flow ratio of the copolymers produced, are as set forth in Table III.

	Runs	Comonomer	TABLE III		
			Melt index g/10 min.	Density g/cm ³	Melt flow ratio
25	9	butene-1	17.8	0.928	29
30	10	propylene	19.2	0.928	25.5
	11	butene-1	29	0.925	23
	12	propylene/butene (50/50)	29	0.927	23

Examples 2 to 5

Each of the polymers of Runs 9 to 12 were molded into dishpans on an 225 g (8 oz.) Impco® molding machine, as described in Example 1, with a cylinder temperature and a gauge pressure approximately 0.69 N/mm² (100 psi) above the minimum pressure to fill the mold, as set forth in Table IV. The low temperature impact strength of the dishpans was measured at -40°C and -51°C (-40°F and -60°F) according to the procedure described in Example 1. The results are set forth in Table IV.

The data shows that articles, such as dishpans, molded from copolymers obtainable as herein described have excellent impact strength.

TABLE IV

Exemple	Resin (run)	Molding conditions				Impact strength Nm (ft./lbs.)	
		Cylinder Temp.		Minimum pressure to fill mold		-40°C (-40°F)	-51°C (-60°F)
		°C	(°F)	N/mm ²	(psi)		
2	9	260	(500)	8.62	(1250)	-	27 (20) (Punctured)
3	10	260	(500)	8.62	(1250)	-	24.8 (18.3) ^m
4	11	204	(400)	7.59	(1100)	34 (25) (Punctured)	28.2 (20.8) (Punctured)
5	12	204	(400)	7.24	(1050)	29.4 (21.7) (Punctured)	25.9 (19.1) (Punctured)

^m 2 out 6 cracked

Examples 6 to 9

Each of the polymers of Runs 9 to 12 were molded into lids on a 85 g (3 oz.) Moslo® injection molding machine, as described in Example 1, with a cylinder temperature and a gauge pressure about 0.83 N/mm² (120 psi) above the minimum pressure to fill the mold, as set forth in Table V. The lids were tested for stress crack resistance in Crisco® oil according to the procedure as described in Example 1. The results are set forth in Table V.

The data shows that articles such as lids produced from the copolymer obtainable as herein described have excellent stress crack resistance.

TABLE V
Molding conditions

Example	Resin (run)	Cylinder temp. °C (°F)	Minimum pressure to fill mold N/mm ² (psi)	Stress crack resistance
6	9	260 (500)	5.69 (825)	> 21 days
7	10	260 (500)	5.69 (825)	> 21 days
8	11	260 (500)	3.8 (550)	> 21 days
9	12	260 (500)	3.8 (550)	> 21 days

Polymerization runs 13 to 17, control products 2 to 4

Butene-1 copolymers of Runs 13 to 17 were prepared according to the procedure of Runs 1 to 8. The density, melt index and secant modulus of the copolymers produced are set forth in Table VI.

The high pressure polyethylene resins of Control Products (C.P.) 2 to 4 were commercially available under the designation PEP 231, 530 and 440 (Union Carbide Corporation).

Run	Comonomer	Density g/cm ³	Melt index g/10 min.	Secant modulus N/mm ²	(psi)
5	13	butene-1	0.918	7.0	221 (32,100)
	14	butene-1	0.926	12.0	283 (41,100)
	15	butene-1	0.928	18.0	335 (48,600)
	16	butene-1	0.928	30.0	336 (48,700)
10	17	butene-1	0.937	7.0	482 (70,000)
	C.P.2	—	0.919	10.0	131 (19,000)
	C.P.3	—	0.924	9.5	172 (25,000)
15	C.P.4	—	0.926	28.0	200 (29,000)

Examples 10 to 14

The resins prepared in Runs 13 to 17 and Control Products 2 to 4 were roto molded into heater ducts. These resins were ground to a powder which passed through a 0.416 mm sieve mesh (U.S. 35 mesh) screen and evaluated in a heater duct mold 17.8 cm (7 inches) wide and 61 cm (24 inches) long with an average wall thickness of 0.32 cm (0.125 inches). The oven temperature was 304°C (580°F), the oven cycle was 12 minutes (except Runs 20 and 21 for which the cycle was 8 minutes) and the mold was cooled by spraying it with cold water for three minutes.

The moldability of each of the resins evaluated was determined. Also, the falling dart impact of each of the samples at -40°C was measured using a 4.5 kg (10 pound) cylindrical dart with a 2.5 cm (1 inch) diameter hemispherical head dropped from 60 cm (2 feet). The percentage of the samples which passed are shown in Table VI. The flex life, as determined in a Ross rubber flex tester with a 90° bend operated at 120 cycles per minute, was also measured for several of these roto molded samples. Environmental stress crack resistance was measured according to the ASTM D1693 bent strip test using 100% Igepal® slit specimens and a temperature of 50°C. This data is shown in Table VII.

The data shows that for a comparable modulus and melt index, the low pressure copolymer resins obtainable as described herein form roto molded parts which are substantially better than the high pressure resins in low temperature impact strength, flex life and stress crack resistance.

TABLE VII

Examples	Low pressure resins					High pressure resins, control products		
	10	11	12	13	14	—	—	—
Resin (Runs)	13	14	15	16	17	2	3	4
Moldability	Exc.	Exc.	Exc.	Exc.	Exc.	Exc.	Exc.	Exc.
% passing 27 Nm (20 ft-lbs) at -40°C	100	100	100	100	100	100	0	0
Flex Life, cycles for 50% failure	150,000	5,000	—	—	—	—	3,000	—
Stress Crack Resistance, Hours for 100% failure	>504	—	15	1	25	4	1	1

Example 15

The butene-1 copolymer resins of Runs 13 to 17 were injection molded into lids and then subjected to the Crisco® oil stress crack resistance test as previously described. No cracking was observed in the bent section

after 21 days of immersion. Under similar conditions lids molded from the high pressure Control Product 1 resin cracked after three minutes.

Example 16

The butene-1 copolymer resins of Runs 14 to 16 were injection molded into dishpans under conditions previously described and then tested for impact strengths at -51°C (-60°F) according to the procedure also previously described. None of the dishpans shattered. Punctures in the dishpan occurred at the number of Nm (foot-pounds) as indicated below in Table VIII. Dishpans molded from the high pressure Control Product 1 resin shattered at 6.8 Nm (5 foot-pound). The data is shown in Table VIII.

TABLE VIII	
Resin run	Impact strength, Nm (ft.-lbs.)
14	35.0 (25.8) (Puncture)
15	27 (20) (Puncture)
16	28.2 (20.8) (Puncture)
Control Product 1	6.8 (5) (Shattered)

Example 17

A butene-1 copolymer (Control product 6) was prepared according to the procedure of Runs 1 to 8. A commercially available high pressure polyethylene, designated DNDA 0180 (Union Carbide Corporation) was used as the control (Control Product 5). Also, included for comparison was the low pressure resin of Run 13 which was higher in melt index than either the butene-1 copolymer or the polyethylene.

The resins were compression molded into test specimens 0.32 cm (0.125 inch) thick according to ASTM D-1928 and tested for stress crack resistance in 100% Igepal® according to the procedure of the ASTM D1693 bent strip test. The time for 50% of 20 molded specimens to crack was determined at 50°C . The results are shown in Table IX.

Resin Type	TABLE IX		
	Control product 6	Control product 5	Run 13
	butene-1 copolymer	high pressure polyethylene	butene-1 copolymer
Melt Index, g/10 min.	1.0	2.0	7.0
Density, g/cm ³	0.921	0.921	0.918
Secant modulus, N/mm ² (psi)	264 (38,300)	158 (23,000)	221 (32,100)
Stress crack resistance (hours for F ₅₀)	>504	200	>504

The results show that even though the low pressure resins are about 50% higher in modulus than the high pressure resin, and hence under more stress in the bent strip test, they are substantially better in stress crack resistance than a high pressure stirred reactor resin which is considered one of the most stress crack resistant commercially available polyethylenes. Even when the melt index of the low pressure resin was increased to 7.0 g/cm³ in the resin of Run 13 the low pressure resin was substantially more stress crack resistant than the high pressure resin having a melt index of 2.0 g/10 min. An increase in melt index normally reduces stress crack resistance.

Claims

1. Use of a low density ethylene hydrocarbon copolymer containing ≥ 90 mol percent of ethylene and ≤ 10 mol percent of propylene and/or butene-1 and having a density of 0.91 to 0.94 g/cm³, a melt index of 7 to 100 g/10 min, a molecular weight distribution M_w/M_n in the range of from 2.7 to 4.1, a total unsaturation group content of from 0.1 to 0.3 C = C/1000 carbon atoms, and a secant modulus of ≥ 2100 to ≤ 5600 bar (≥ 30000 to ≤ 80000 psi), and obtainable by copolymerizing ethylene with propylene and/or butene-1 at a temperature of from about 30 to 115°C in a gas phase containing from 0 to 2.0 moles of hydrogen per mol of ethylene in the presence of particles of an activated precursor composition, wherein said precursor composition has the formula



wherein

m is ≥ 1.5 to ≤ 56

n is 0 or 1

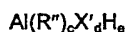
p is ≥ 6 to ≤ 116

q is ≥ 2 to ≤ 85

R is a C₁ to C₁₄ aliphatic or aromatic hydrocarbon radical, or COR', wherein R' is a C₁ to C₁₄ aliphatic or aromatic hydrocarbon radical,

X is selected from the group consisting of Cl, Br, I or mixtures thereof ;

ED is a liquid organic electron donor compound in which said precursor composition and the Ti and Mg components thereof are soluble and which is selected from the group consisting of alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ethers, cyclic ethers and aliphatic ketones, said precursor composition having an average particle size of 10 to 100 μm , a bulk density of 0.29 to 0.53 g/cm³, and being mechanically mixed or blended with at least one solid inert carrier material in a ratio of 0.033 to 1 part of precursor composition per part by weight carrier material, and being activated with an activator compound having the formula



wherein X' is Cl or OR''', R'' and R''' are the same or different and are C₁ to C₁₄ saturated hydrocarbon radicals, d is 0 to 1.5,

e is 0 or 1, and

c + d + e = 3 which polymerization is conducted continuously in a gas phase fluid bed reaction zone under a pressure of < 69 bar (< 1000 psi), and said precursor composition is partially activated with > 0 to < 10 mols of activator compound per mol of titanium compound in said precursor composition in a hydrocarbon slurry prior to feeding of the precursor composition to said reaction zone, dried to obtain a free-flowing solid particulate material, and then being completely activated in said reaction zone with > 10 up to a total of < 400 mols of activator compound per mol of titanium compound in said precursor composition, said complete activation being effected by spraying additional activator compound into the reactor in the form of a solution in a hydrocarbon containing 2 to 30 weight percent of the activator compound, or absorbed on a carrier material containing 10 to 50 weight percent of the activator compound ;
for preparing articles by injection molding and roto molding.

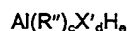
2. Use of a copolymer as defined in claim 1, having a density of > 0.918 to < 0.935 g/cm³ and a melt index of 7 to 80 g/10 min for the purpose indicated in claim 1.

Ansprüche

1. Verwendung eines niedrig dichten Kohlenwasserstoffcopolymerisats das ≥ 90 Mol-% Ethylen und ≤ 10 Mol-% Propylen und/oder Buten-1 enthält und eine Dichte von 0,91 bis 0,94 g/cm³, eine Molekulargewichtsverteilung M_w/M_n im Bereich von 2,7 bis 4,1, einen Gesamtgehalt an ungesättigten Gruppen von 0,1 bis 0,3 C = C/1000 Kohlenstoffatomen und einen Sekantenmodul von ≥ 2100 bis ≤ 5600 bar (≥ 30000 bis ≤ 80000 psi) hat und erhältlich ist, indem man Ethylen mit Propylen und/oder Buten-1 bei einer Temperatur von etwa 30 bis 115°C in einer 0 bis 2,0 Mol Wasserstoff pro Mol Ethylen enthaltenden Gasphase in Anwesenheit von Teilchen einer aktivierten Vorläuferzusammensetzung copolymerisiert, worin diese Vorläuferzusammensetzung die Formel



- hat in welcher
 $m \geq 1,5$ bis ≤ 56 ist,
 n 0 oder 1 ist,
 5 $p \geq 6$ bis ≤ 116 ist,
 $p \geq 2$ bis ≤ 85 ist,
 R ein C_1 - C_{14} aliphatischer oder aromatischer Kohlenwasserstoffrest oder COR' ist, worin R' ein C_1 - C_{14} aliphatischer oder aromatischer Kohlenwasserstoffrest ist,
 X aus der aus Cl, Br, J oder Mischungen derselben bestehenden Gruppe ausgewählt ist,
 10 ED eine flüssige organische Elektronendonator-Verbindung ist, in welcher die Vorläuferzusammensetzung und die Ti und Mg Komponenten derselben löslich sind und die ausgewählt ist aus der Gruppe, die aus Alkylestem aliphatischer und aromatischer Carbonsäuren, aliphatischen Ethern, cyclischen Ethern und aliphatischen Ketonen besteht,
 wobei dieses Vorläuferzusammensetzung eine durchschnittliche Teilchengröße von 10 bis 100 μm , eine
 15 Schüttdichte von 0,29 bis 0,53 g/cm³ hat und mechanisch mit mindestens einem festen inerten Trägermaterial in einem Verhältnis von 0,033 bis 1 Teil Vorläuferzusammensetzung pro Gewichtsteil Trägermaterial geodermisch vermischt und mit einer Aktivatorverbindung der Formel aktiviert ist



- 20 in welcher
 X' für Cl oder OR''' steht, R'' und R''' gleich oder verschieden und C_1 - C_{14} gesättigte Kohlenwasserstoffreste bedeuten,
 $d = 0$ bis 1,5 ist,
 25 $e = 0$ oder 1 ist und
 $c + d + e = 3$ ist,
 wobei die Polymerisation kontinuierlich in einer Gasphasen-Wirbelbetreaktionszone unter einem Druck von < 69 bar (< 1000 psi) durchgeführt wird und die Vorläuferzusammensetzung teilweise mit > 0 bis < 10 Mol Aktivatorverbindung pro Mol Titanverbindung in der Vorläuferzusammensetzung in einer Kohlenwasserstoffaufschlammung aktiviert wird, bevor die Vorläuferzusammensetzung in diese Reaktionszone eingeführt wird, zur
 30 Bildung eines frei fließenden festen fein zerteilten Materials getrocknet und dann in dieser Reaktionszone mit ≥ 10 bis zu insgesamt ≤ 400 Mol Aktivatorverbindung pro Mol Titanverbindung in der Vorläuferzusammensetzung vollständig aktiviert wird, wobei diese vollständige Aktivierung durchgeführt wird, indem in den Reaktor in Form einer Lösung in einem Kohlenwasserstoff, die 2 bis 30 Gew.-% Aktivatorverbindung enthält, oder absorbiert auf einem Trägermaterial, das 10 bis 50 Gew.-% der Aktivatorverbindung enthält, zusätzliche Aktivatorverbindung eingesprüht wird, zur Herstellung von Formkörpern nach dem Spritzgieß- oder Rotationsgießverfahren.

2. Verwendung eines Copolymerisats gemäß Anspruch 1 mit einer Dichte von $\geq 0,918$ bis $\leq 0,935$ g/cm³ und einem Schmelzindex von ≥ 7 bis ≤ 80 g/10 min für den in Anspruch 1 angegebenen Zweck.

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Revendications

1. Utilisation d'un copolymère d'un hydrocarbure et d'éthylène basse densité contenant une quantité supérieure ou égale à 90 moles pour cent d'éthylène et une quantité inférieure ou égale à 10 moles pour cent de propylène et/ou de butène-1 et ayant une masse volumique de 0,91 à 0,94 g/cm³, un indice de fluidité de 7 à 100 g/10 min, une distribution de poids moléculaire M_p/M_n comprise dans l'intervalle de 2,7 à 4,1, une teneur totale en groupes à insaturation de 0,1 à 0,3 C = C/1000 atomes de carbone et un module sécante allant d'une valeur supérieure ou égale à 2100 à une valeur inférieure ou égale à 5600 bars (≥ 30000 à ≤ 80000 lb/in²) et
 50 pouvant être obtenu par copolymérisation d'éthylène avec le propylène et/ou le butène-1 à une température d'environ 30 à 115°C dans une phase gazeuse contenant 0 à 2,0 moles d'hydrogène par mole d'éthylène en présence de particules d'une composition de précurseur activé, la composition de précurseur répondant à la formule



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dans laquelle m va d'une valeur supérieure ou égale à 1,5 à une valeur inférieure ou égale à 56, n est égal à 0 ou à 1,

p va d'une valeur supérieure ou égale à 6 à une valeur inférieure ou égale à 116,

q va d'une valeur supérieure ou égale à 2 à une valeur inférieure ou égale à 85,

R est un radical d'hydrocarbure aliphatique ou aromatique en C₁ à C₁₄, ou est un groupe COR' dans lequel R' est un radical d'hydrocarbure aliphatique ou aromatique en C₁ à C₁₄,

5 X est choisi dans le groupe comprenant Cl, Br, I ou leurs mélanges,

DE est un composé organique liquide donneur d'électrons dans lequel la composition de précurseur et ses composants Ti et Mg sont solubles et que l'on choisit dans le groupe comprenant des esters alkyliques d'acides carboxyliques aliphatiques et aromatiques, des éthers aliphatiques, des éthers cycliques et des cétones aliphatiques,

10 ladite composition de précurseur ayant un diamètre moyen des particules de 10 à 100 µm, une densité apparente de 0,29 à 0,53 g/cm³, et étant mécaniquement mélangée ou malaxée avec au moins un support inerte solide dans un rapport de 0,033 à 1 partie de composition de précurseur par partie en poids de matière de support, et étant activée avec un composé activateur répondant à la formule :



dans laquelle X' représente Cl ou un groupe OR''', R'' et R''' sont égaux ou différents et sont des radicaux hydrocarbonés saturés en C₁ à C₁₄,

d a une valeur de 0 à 1,5,

20 e est égal à 0 ou à 1, et

la somme c + d + e est égale à 3,

cette polymérisation étant conduite en continu dans une zone de réaction à lit fluide en phase gazeuse sous une pression inférieure à 69 bars (< 1000 lb/in²) et ladite composition de précurseur étant partiellement activée avec une quantité allant de plus de 0 à moins de 10 moles de composé activateur par mole de composé de

25 titane dans ladite composition de précurseur en suspension dans un hydrocarbure avant l'arrivée de la composition de précurseur dans ladite zone de réaction, séchée pour obtenir une matière en particules solides s'écoulant librement, puis complètement activée dans ladite zone de réaction avec une quantité allant d'une valeur supérieure ou égale à 10 à un total inférieur ou égal à 400 moles de composé activateur par mole de composé de titane dans ladite composition de précurseur, ladite activation totale étant effectuée par pulvérisation d'une quantité additionnelle d'activateur dans le réacteur sous la forme d'une solution dans un hydrocarbure contenant 2 à 30% en poids du composé activateur, ou absorbée sur une matière de support contenant 10 à 50% en poids dudit composé activateur ;

pour la préparation d'articles par moulage par injection et moulage rotatif.

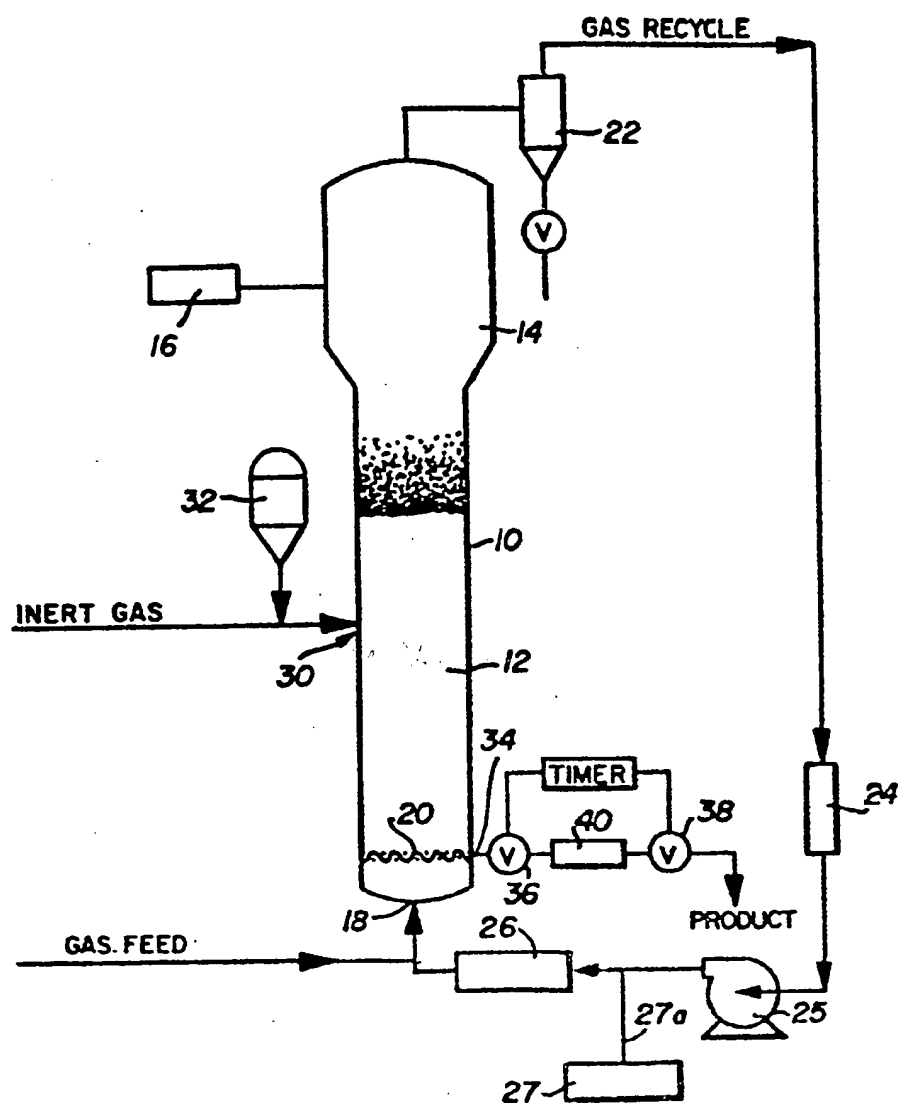
35 2. Utilisation d'un copolymère tel que défini dans la revendication 1, de masse volumique allant d'une valeur supérieure ou égale à 0,918 à une valeur inférieure ou égale à 0,935 g/cm³ et d'indice de fluidité allant de 7 à 80 g/10 min, pour le but indiqué dans la revendication 1.

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